BACTERIAL MINERALIZATION OF AZO DYE TREATED BY NANOSTRUCTURED TITANIUM DIOXIDE

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ABSTRACT. A sequential aerobic treatment process based of mixed bacterial population from active sludge has been applied to mineralize azo dyes, which is preliminary oxidized and destructed by sprayed nanostructured titanium dioxide. Samples of treated Reactive Black 5 in bacterial suspensions were centrifuged and analyzed by UV-VIS spectrophotometer. Thus, the mineralization of investigated azo dye was measured. The results showed that aerobic biological system in active sludge has higher efficiency for purification of dye treated with nanostructured TiO_2 than untreated one.

БАКТЕРИАЛНО МИНЕРАЛИЗИРАНЕ НА АЗО БАГРИЛА ТРТИРАНИ С НАНОСТРУКТУРИРАН ТИТАНИЕВ ДИОКСИД

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РЕЗЮМЕ. Аеробен процес за третиране, базиран на смесени бактериални популации от активна утайка, беше приложен за минерализиране на азо багрило, което предварително е окислено и разрушено посредством наноструктуриран титаниев диоксид. Образци от третирано багрило реактивно черно 5 бяха центрафугирани и анализирани с ултравиолетов спектрофотометър. По този начин минерализацията на изследваното азо багрило беше измерена. Резултатите показват, че аеробните биологични системи в активна утайка притежават висока ефективност за пречистване на багрило, което е третирано с наноструктуриран TiO_2, отколкото нетретирано багрило.

1. Introduction

Tanneries factories are important user of dyes, an important source of pollution, especially in some countries, high leather producers, like China and North African countries. Processes for the treatment of heavy metals, like chromium or cadmium, which often accompanies dyes, are now well known and controlled. Owing to their colouration, the dyes cause floral pollution and aesthetic pollution (even a small amount of dye is clearly apparent). However, even if dyes are not toxic, the toxicity of their by-products has to be considered. Indeed, dyes degradation led to aromatic amines, which are known to be toxic.

Decolorization of azo dyestuffs by sequential reactions involves the degradation of azo dye by reduction or cleavage of azo bond by anaerobic digestion and ultimate biotransformation of aromatic amines in aerobic conditions. The limited past investigations have shown that azo dyes can be completely decolorized and some intermediates such as aromatic amines with side groups (-Cl, -OH, $-SO_3$, -COOH) containing metabolites were quantitatively detected (O'Neil et al., 2000; Luangdilok and Panswad 2000; Van Der Zee et al., 2003). In most cases the azo dyes are resistant to biodegradation under aerobic conditions (Pagga and Brown 1986; Jimenez et al., 1988; Shaul et al., 1991; Ganesh et al., 1994; Pagga 1994), but they undergo reductive fission of the azo linkage relatively easily under anaerobic conditions (Brown 1981; Brown and Laboureur 1983; Carliell et al., 1994;Razo-Flores et al., 1997; Beydilli et al., 1998). Among the advanced oxidative processes, heterogeneous photocatalysis appears as an interesting technique for the treatment of endogenic organic pollutions. Indeed, titan dioxide (TiO_2) activation under UV irradiation (λ < 390 nm) allows the generation from water or hydroxide ions of free radicals •OH, highly reactive. These free radicals can then react with the persistent components adsorbed at the surface of titan dioxide until their total mineralization. The ambient temperature and the possible use of solar UV are the photocatalysis advantages; moreover titan dioxide is not toxic. A long period of time can be required for the disappearance of the active molecule and its complete mineralization during photocatalytic degradation. Due to this reason the process is significantly costly. We propose an integration of two processes: photocatalysis and biological treatment treatment in order to reduce the costs. In this paper are therefore presented preliminary results concerning the degradation of the azo dye Reactive Black 5 used in Moroccan tannery factories by means of an integrated process involving photocatalysis UV/TiO_2 followed by biological treatment with active sludge.

2. Experimental procedures

2.1. Photocatalytic decolorization of Reactive Black 5 by nanostructured TiO_2.

To prepare oxidized and destructed azo dyes was used the procedure as follow. Stock solution of 30 mg/L RB5 was prepared with pH = 2.70. Aliquot of 150 ml was transferred in a reaction vessel. It was kept 30 min at dark under in the presence of nanostructured TiO_2 catalyst, aeration and energetic mixing by magnetic stirrer. After completing the dark phase the reaction mixture was irradiated by UV lamp with maximum emission at 370 nm and light intensity 5_x10^{-5} W/cm^2. After three hours photocatalytic treatment the obtained mixture contains almost benzene derivatives as byproducts and negligible small amount of RB5. This mixture (solution 1) was used future for biological treatment by active sludge.

2.1. Biological treatment of Reactive Black 5 byproducts by active sludge.

500 ml preculture medium contained: 10 g glucose, 0.5 g NH_4Cl, 0.25 g $MgSO_4$, 0.25 g K_2HPO_4, 0,005 g $CaCl_2$ and 0.005 g Na_2HPO_4 (solution 2). 15 ml of solution 2 was dissolved into solution to obtain a volume of 150 ml. This final solution 3 was inoculated with microbiological suspension from active sludge. The final suspension was shaking at temperature 30 ˚C for 2 days. Aliquots of 2 ml were taken at every 6 hours, centrifuged and analyzed by UV-spectrophotometer.

3. Result and discussion

Time course of dye decoloration reaction was followed at fixed absorption maximum of 600 nm. Figure 1 shows the plot of decomposition vs time of the azo-group or RB 5 at fixed concentration. It exhibited first-order kinetics and, plot C/C_0 versus time (where C_0 and C are initial concentration and concentration of the photolyzed solution at time *t*, respectively) displayed excellent single exponential fit.

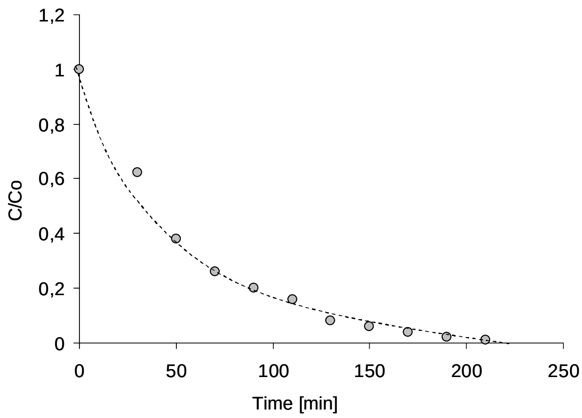

Fig. 1. First-order kinetic trace for the photocatalytic decoloration of Reactive Black 5 at pH = 2.7

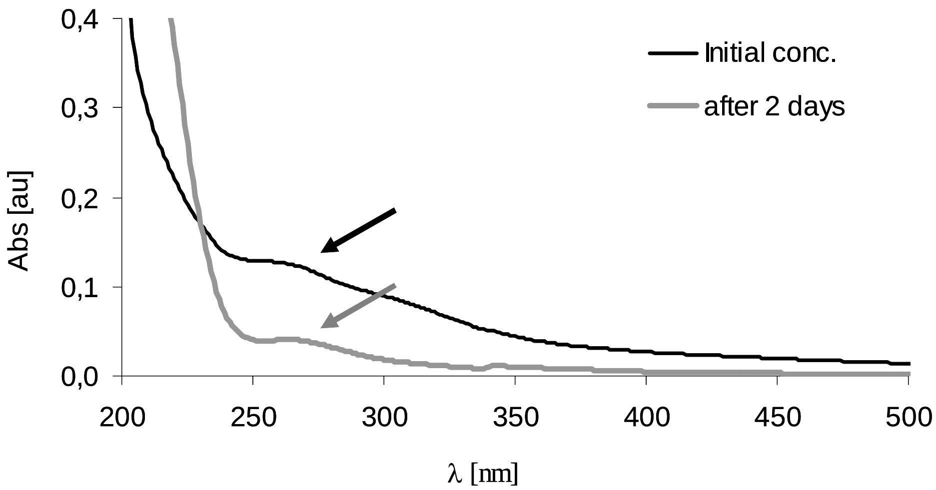

Fig. 2. Absorption spectra of aromatic byproducts of RB5 (pointed with arrows) before and after two days biological treatment by active sludge

From Fig. 1 it might conclude that after 3 hours photocatalytic treatment with TiO_2 the molecules of RB5 are > 95 %. However, the reaction mixture (solution 1) contains a mixture of aromatic byproducts, which are mainly derivatives of benzene. They have an absorption maximum at 255 nm (as it is shown on Fig. 2). The solution 2 was dissolved (ten times) in solution 1 to obtain an appropriate culture medium for grown of microbiological suspension in active sludge. The importance of this medium is that it does not contains any organic as proteins or yeast extract, which masked the pointed with arrows peak in Fig. 2 corresponding to the RB5 byproducts derivatives. Thus is possible the monitoring of their concentration removal from bacterial suspension only by use of higher sensitive UV-spectrophotometer, but not other analytical tool. Only glucose was present in the culture medium as organic source of energy, but it does not affect the peak at 255 nm. However, we found that even at low concentration, the presence of glucose favored byproducts biodegradation, which was recorded throughout culture. As it is seen from Fig. 2 after 2 days treatment more than 80 % of the byproducts amount is reduced.

On Fig. 3 is shown a light microscopic image of bacterial suspension, which is isolated from the active sludge. Most of the bacteria are with size 1-2 μm and rod shape. The calculated concentration of bacteria was 2.3_x10^8 cell/ml.

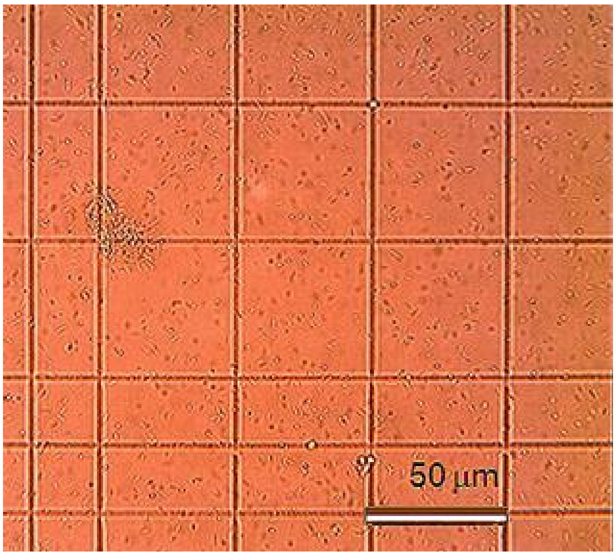

Fig. 3. Light microscopic image of bacterial suspension in aerobic active sludge

4. Conclusion

In this work we achieved removal of the byproducts from photocatalytic oxidation of Reactive Black 5 by microbial suspension of active sludge. The purification process was completed after 2 days treatment. The method is low cost in comparison with the congenital methods, and can be integrated with the photocatalytic treatment by nanostructured oxides. This approach opens great opportunities for modernization and future application in many industrial purification facilities.

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